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硕士学位论文

厦门湾海水-沉积物系统中 PCDD/Fs 的含量、多相分配及颗粒垂直通量研究

Concentration, Multi-phase Partitioning and Vertical Fluxes of PCDD/Fs in Seawater-Sediment System of Xiamen Bay

洪清泉

指导教师姓名：蔡明刚　副教授
专　业　名　称：海　洋　化　学

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摘要

于 2011 年 12 月采集了厦门湾海水、沉积物样品，开展海水-沉积物系统中多氯代二苯并二噁英/呋喃（Polychlorinated dibenzo-*p*-dioxins and dibenzofurans，PCDD/Fs）的多相分配及颗粒垂直通量研究。首次获得 PCDD/Fs 在厦门湾海水中悬浮颗粒态、胶体态（DOC 吸附态）和自由溶解态的含量、水平与垂直分布，沉积物中 PCDD/Fs 的时空分布，PCDD/Fs 的来源和海水-沉积物界面颗粒态 PCDD/Fs 的垂直交换通量等特征，提升了对海洋环境中 PCDD/Fs 的多相分配和颗粒垂直交换过程的认识。取得了以下成果：

厦门湾水体中 17 种 PCDD/Fs 的总含量（PCDD/Fs）为 35.389-283.933 pg/L，平均为 145.156 pg/L。其中，PCDDs 含量为 34.929-282.554 pg/L，占 PCDD/Fs 的 98.6-99.6%。总体上，厦门湾水体中的 PCDD/Fs 含量处于较高水平。水体中 PCDD/Fs 的总毒性当量（采用 WHO 2005 年的毒性当量因子体系计算）为 0.084-0.422 pg TEQ/L（平均为 0.250 pg TEQ/L），超过美国 EPA 规定的水质标准（0.14 pg TEQ/L）。其中，对毒性当量贡献最大的为 1,2,3,7,8-P_5CDD，其次为 O_8CDD 和 1,2,3,4,6,7,8-H_7CDD。

表层水体中 PCDD/Fs 的含量随着与九龙江口距离的增大而减小，表明九龙江水体输入是研究区域 PCDD/Fs 的主要输入途径。垂直水体中 PCDD/Fs 呈现上层水体和底层水体含量较高而中层水体含量较低的分布，主要与载带 PCDD/Fs 的悬浮颗粒物在水体中的迁移有关。上层水体主要载带大量颗粒物的九龙江水体输入，因而具有较高的 PCDD/Fs 含量，底层水体则主要由于沉积物的再悬浮作用从沉积物释放颗粒态 PCDD/Fs。

水体中的 PCDD/Fs 在悬浮颗粒态-胶体态-自由溶解态三相间主要以悬浮颗粒态存在，占 98.4-99.7%，PCDD/Fs 在颗粒物与表观溶解态间的分配接近平衡。PCDD/Fs 在三相间的分配是温度、盐度、pH、Chl-*a*、DOC、SPM、POC/SPM 等因素共同作用的结果。其中，POC/SPM、Chl-*a*、pH 和 DOC 主要控制胶体态和自由溶解态间的分配，SPM 主要控制颗粒态的含量与分配。

厦门湾沉积物 PCDD/Fs 的含量为 1 129.656-3 806.936 pg/g d.w.，平均含量为 1 809.188 pg/g d.w.，总毒性当量为 1.60-6.65 pg TEQ/g，平均为 2.49 pg TEQ/g，

其毒性当量主要以五至八氯代的 PCDDs 贡献为主。根据 Hemming 等（2003）提出的生物毒性风险评价标准，厦门湾表层沉积物中 PCDD/Fs 含量对生物没有毒性风险。沉积物中 PCDD/Fs 含量与沉积物中的细颗粒（粘土、粉砂）和 TOC 含量存在正相关关系，说明沉积物中 PCDD/Fs 主要受细颗粒和 TOC 吸附作用控制。

表层沉积物中 PCDD/Fs 的分布与水体中颗粒态 PCDD/Fs 的分布相似，从河端至海端逐渐降低，说明九龙江水体载带的颗粒态 PCDD/Fs 往外海迁移过程中的沉降和埋藏是沉积物中 PCDD/Fs 的主要来源。对柱状沉积物的研究表明，在百年时间尺度上，PCDD/Fs 呈现波动变化，最大值出现在 1970 年代，时间变化主要与 PCP 等化学品的生产与使用的变化有关。

海水和沉积物中 PCDD/Fs 的同系物组成相似，均以 O_8CDD 为主，其次为 H_7CDD，另有少量 O_8CDF 和 H_7CDF。结合主成分分析和聚类分析，判断厦门湾 PCDD/F 的主要来源是 PCP 及其钠盐使用过程中杂质所含的 PCDD/Fs 的排放及污水污泥的输入，其主要输入途径是通过污水污泥汇入九龙江水体，并随九龙江水体输送，大气沉降所占的比例很小。百年时间尺度上，PCDD/Fs 的同系物组成几乎不变，说明近 100 年内，PCDD/Fs 降解作用不显著。

对海水-沉积物界面颗粒 PCDD/Fs 的垂直交换通量估算表明，水平输送和沉积物的埋藏作用是 PCDD/Fs 从海水-沉积物界面输出的主要过程。在扩散作用和降解作用可以忽略的条件下，河口区沉积物再悬浮通量不能忽略，证明了河口区沉积物为 PCDD/Fs 的“二次污染源”。

关键词： 二噁英；海水-沉积物；多相分配；通量；埋藏与再悬浮；厦门湾

ABSTRACT

Seawater and sediment samples in the Xiamen Bay were collected in December, 2011, aiming to study the multi-phase partitioning and vertical fluxes of particle bounded polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in an estuarine seawater-sediment system. It's the first time to report the partitioning between particulate-colloidal (DOC bounded)-freely dissolved phase, horizontal and vertical distribution pattern in seawater, spatial and temporal distribution in sediment and vertical fluxes of particle particle bounded PCDD/Fs. It makes a great improvement in understanding the particulate dynamics and multi-phase behavior of PCDD/Fs in marine environment. Main conclusions are as followed:

The sum concentrations of seventeen PCDD/F congeners in seawater of the Xiamen Bay were ranged in 35.389-283.933 pg/L (averaged in 145.156 pg/L), which means they were in the higher end of the PCDD/Fs levels all over the world. The sum concentrations of PCDDs were ranged in 34.929-282.554 pg/L, contributing 98.6-99.6% of PCDD/Fs. The TEQ (calculated with the WHO 2005 Toxic Equivalency Factors) were in the range of 0.084 to 0.422 pg TEQ/L, with an average of 0.250 pg TEQ/L. This means the TEQ in seawater of the Xiamen Bay exceed the water quality criteria recommended by USEPA. Contribution to TEQ for congeners was in the order: 1,2,3,7,8-P_5CDD>O_8CDD>1,2,3,4,6,7,8-H_7CDD.

The concentrations in the surface seawater decreased with the distance from the Jiulong River Estuary, indicating a potential input from the river. Lower concentrations existed in the median layer of the seawater, while higher ones distributed in the surface and the bottom seawater in the vertical profile. This involved the transport of particles bounded PCDD/Fs in water column. A large amount of particle containing PCDD/Fs was input from the Jiulong River, leading to the higher concentrations in the surface seawater while the resuspension of sediment resulted to higher concentrations in the bottom seawater

A three-phase (particulate-colloidal-freely dissolved phase) partitioning model

was applied and found that prticle bounded PCDD/Fs contributed 98.4-99.7% of the PCDD/Fs in seawater. The distribution between particulate and apparently dissovled phase was found to be near or at equilibrium. The partition in the three-phase system may result from a combination of the effects of temperature, salinity, pH, Chl-*a*, DOC, SPM and POC/SPM. The content and partitioning in the particles was dominated by SPM, while the partitioning between the colloidal phase and freely dissovled phase was controll by the combined effects of POC/SPM, Chl-*a*, pH and DOC.

The concentrations and TEQ of PCDD/Fs in the sediment of Xiamen Bay were ranged in 1 129.656-3 806.936 pg/g d.w. (averaged in 1 809.188 pg/g d.w. and 1.60-6.65 pg TEQ/g d.w. (averaged in 2.49 pg TEQ/g), respectively. The TEQ was mainly contributed by *penta*- to *octa*- chlorinated congeners, which caused no risk to organisms. Significant positive relationships between fine-grained sediments, organic carbon and PCDD/Fs indicated that sorption of PCDD/Fs to organic matter and fine particles dominates the fate of PCDD/Fs in the sediments.

The PCDD/Fs in the surface sediments demonstrated a similar distribution with that in the surface seawater, decreasing from the Jiulong River Estuary to the outer of the bay, which implied a deposition and burial of particlate PCDD/Fs from overlying seawater. The temporal distribution in the core sediment fluctuated in the time scale of 100 years, with a maximun in the 1970s, which was due to the change in the manufacture and use of chemicals such as PCP.

Similar congener patterns in the seawater and sediment were found to be dominated by O_8CDD, which is followed by H_7CDD and minor O_8CDF and H_7CDF. The congener patterns, combined with the results of Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA), indicated a potential major source from the impurity of PCP (Pentachlorophenol)+its sodium and sewage sludge. The main path is the input of sewage sludge and the transport of Jiulong River water. The congener pattern did not change over 100 years, implying essentially zero degradation had occurred in the environment.

The estimated vertical fluxes of particulate PCDD/Fs in the seawater-sediment interface indicated that horizontal transport and sediment burial are the dominant

export processes. Wihout the consideration of diffision and degradation, the resuspension flux should not be ignored in estuary which makes estuarine sediments potential secondary source of PCDD/Fs.

Keywords: Dioxin; Seawater-sediment; Multi-Phase Partitioning; Flux; Burial and Resuspension; Xiamen Bay